

FUEL PROCESSOR INTEGRATED H₂S CATALYTIC PARTIAL OXIDATION TECHNOLOGY FOR SULFUR REMOVAL IN FUEL CELL POWER PLANTS

Todd H. Gardner, David A. Berry, K. David Lyons,
Michael J. Monahan and Robert E. James III

U. S. Department of Energy
National Energy Technology Laboratory
3610 Collins Ferry Road
Morgantown, WV 26507-0880

Introduction

Fuel cell applications utilizing transportation fuels, military logistic fuels, coal, propane and natural gas as feedstocks require the development of fuel processors that incorporate integrated desulfurization technology. These feedstocks may contain as little as 2.29×10^{-4} kg/m³ total sulfur, as in pipeline natural gas,¹ to 0.3 weight percent total sulfur, as in military JP-8 fuel,² to several percent total sulfur as is present in some coals. If sorbent-based technology is to be used for sulfur removal, then the quantity of sulfur present in the feedstock will greatly effect the fuel processor's footprint and its sorbent change out interval.

An alternative to sorbent-based technology is to catalytically convert the H₂S present in these feedstocks directly to elemental sulfur. The product sulfur may then be separated and recovered from the fuel gas as a solid precipitate. This technology is known as H₂S selective catalytic partial oxidation. The chemistry behind this process is simple:



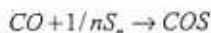
Here, *n* represents the various polymers of sulfur that may possibly be formed (*n* = 2, 6, 8).

There are numerous reports in the literature of low temperature H₂S catalytic partial oxidation technology being applied to natural gas processing systems.^{3,4,5} More recent attention has turned to coal-derived synthesis gas desulfurization.⁶ With liquid fuels, no research has yet been reported.

An additional complexity with many fuel cell feedstocks is that the sulfur compounds present are in the form of organic sulfur. Therefore, a hydrodesulfurization reactor is necessary to first convert these organic sulfur compounds into H₂S. This implies that a H₂ recycle back to the hydrodesulfurizer would be necessary.

In the case where liquid fuels will be desulfurized, the H₂S present cannot be directly oxidized in the presence of higher hydrocarbons (C₄+) due to their high oxidation potential.⁷ Therefore, the liquid fuel must first be liberated of H₂S through stripping. Here, we propose using H₂ as an H₂S stripping gas. Thermodynamic calculations indicate that H₂S is significantly more soluble in the H₂ gas phase than the liquid higher hydrocarbon phase.

For the special case when synthesis gases are to be desulfurized, such as coal-derived synthesis gas, the desulfurization reaction must be conducted at a sufficiently low enough temperature to avoid the side reaction:



In the present work, we report on the ability of activated carbon to function as an oxidation catalyst, selectively oxidizing H₂S directly to elemental sulfur. Three different fuel cell feedstocks were considered: natural gas, middle distillates and coal-derived synthesis gases. The ability for this process and this catalyst to produce a sweetened fuel cell feedstock is discussed.

Experimental

Apparatus. Catalyst experiments were conducted in a laboratory scale, fixed-bed reactor: 1.16 m long by 1.05 cm internal diameter made of quartz glass. Quartz wool was used as a distributor to support the catalyst. The reactor was vertically positioned in a Lindburg single zone furnace (model No. 56447) in the down flow mode. Reaction temperature was measured by an externally located K-type thermocouple axially positioned at the middle of the fixed-bed. The different fuel gas mixtures were derived by manifolded individual bottled gases supplied by Matheson. Individual gas flow rates were controlled using MKS mass flow controllers (model No. 1159B) coupled with an MKS power supply (model No. 247C).

Catalyst Properties. The activated carbon catalyst used in the study was Calgon Centaur 4x6 granular activated carbon. The N₂ BET surface area was 662 m²/g. Catalyst loss on attrition was 10.5 percent by ASTM D4058-92. Its moisture content was determined to be 4.15 weight percent.

Analytical Methods. H₂S, COS, CS₂ and SO₂ were analyzed using four separate gas chromatographs. Low concentrations of H₂S, zero to approximately 150 ppmv, were analyzed using a glass column 1/8" x 6' packed with (40/60 mesh) Carboxpack BHT 100. The column was used in a Perkin Elmer Sigma 300 gas chromatograph equipped with a Flame Photometric Detector (FPD). Low concentrations of SO₂, zero to approximately 1500 ppmv, were analyzed using a teflon column 1/8" x 8' packed with Chromosil 310. The column was used in Perkin Elmer 8500 gas chromatograph equipped with a FPD. COS and CS₂ were analyzed using a teflon column 1/8" x 8' packed with Chromosil 310. The column was used in a Perkin Elmer AutoSystem gas chromatograph equipped with a FPD. Gas analyses reported in this investigation were taken one hour after steady state conditions were achieved.

Results and Discussion

Natural Gas Desulfurization. In this experiment, an activated carbon's ability to selectively oxidize H₂S to elemental sulfur in a CH₄/H₂S mixture was studied. This experiment was conducted at a GHSV of 2,500 h⁻¹ at 157 kPa with 500 ppmv of H₂S with the balance methane. At the inlet, sufficient air was injected to achieve an H₂S:O₂ ratio of 1:2. CH₄ co-oxidation did not take place under these conditions. From Figure 1, very high conversions (>99.9%) of H₂S were achieved over the temperature range 105 to 145°C. SO₂ evolution was observed at temperatures greater than 125°C. This probably occurred due to over oxidation of sulfur product in the pores of the catalyst. Presumably, a larger pore size would allow the product sulfur to desorb from the catalyst surface, rather than being trapped by capillary forces, mitigating this over-oxidation tendency at such low temperatures. Total sulfur levels were maintained below 0.6 ppmv in the temperature range between 105 and 125°C.

Middle Distillate Desulfurization. As discussed earlier, H₂ was used to strip liquid fuels of dissolved H₂S. Therefore, the objective of this experiment was to assess activated carbon's ability to selectively oxidize H₂S to elemental sulfur in a H₂/H₂S mixture. This experiment was conducted at a GHSV of 2,500 h⁻¹ at 157 kPa with 15,000 ppmv of H₂S in 78 Vol. % H₂ and 20.5 Vol. % N₂. At the inlet sufficient air was injected to achieve an H₂S:O₂ ratio of 2:1. H₂ co-oxidation did not take place under these conditions. From Figure 2, we observe a very high sulfur selectivity (>99.9%), but with relatively modest H₂S and O₂ conversions over the temperature range 135 to 175°C. From a process standpoint, the complete removal of H₂S at this stage would be unnecessary and, in fact, undesirable since the hydrodesulfurization catalyst is active only in the sulfide state.

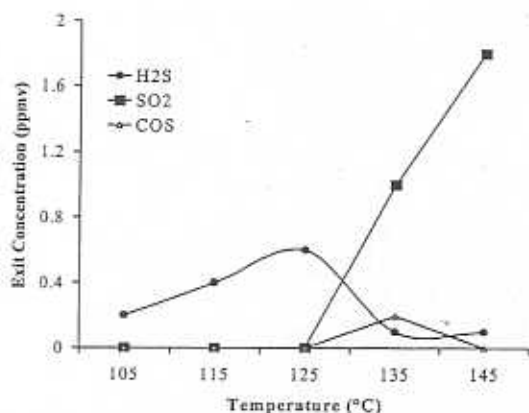


Figure 1. Sulfur exit concentrations from the desulfurizer for H₂S, SO₂, COS. Inlet conditions were methane gas with 500 ppmv H₂S at the inlet. H₂S:O₂ was 1:2, GHSV was 2,500 h⁻¹.

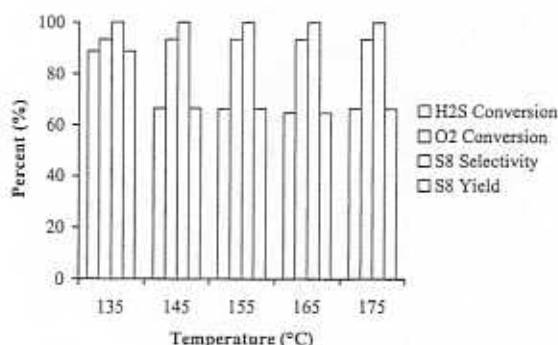


Figure 2. H₂S and O₂ conversion and sulfur selectivity from the desulfurizer. Inlet conditions were 1.5 Vol. % H₂S, 78 Vol. % H₂ and 20.5 Vol. % N₂. H₂S:O₂ was 2:1, GHSV was 2,500 h⁻¹.

However, to avoid accumulation in a recycle loop, O₂ and H₂S conversions would need to be higher.

Coal-Derived Synthesis Gas Desulfurization. The exit temperature after the water quench in a Texaco O₂-blown IGCC power plant is approximately 120 to 145°C. Desulfurization at this point is crucial to protect down stream power generation equipment including fuel cells. Our laboratory tested activated carbon's ability to catalyze H₂S directly into elemental sulfur while in the presence of a coal-derived synthesis gas. This experiment was conducted at a GHSV of 2,500 h⁻¹ at 157 kPa with 1,000 ppmv H₂S in a simulated Texaco O₂-blown gasifier gas (36 Vol. % CO, 27 Vol. % H₂, 18 Vol. % H₂O, 5.9 Vol. % N₂, 13 Vol. % CO₂). At the inlet, sufficient air was injected to achieve an H₂S:O₂ ratio of 1:5. H₂ and CO co-oxidation did not take place. From Figure 3, we observed that H₂S and SO₂ levels at all temperatures investigated remained below 1.0 ppmv, however, above 145°C CO began reacting with the sulfur product to produce COS. Figure 4 was an x-ray diffraction pattern of one of the activated catalyst pellets from this experiment. It demonstrated that the sulfur accumulating within the activated carbon catalyst pores was in the form of orthorhombic sulfur, S₈.

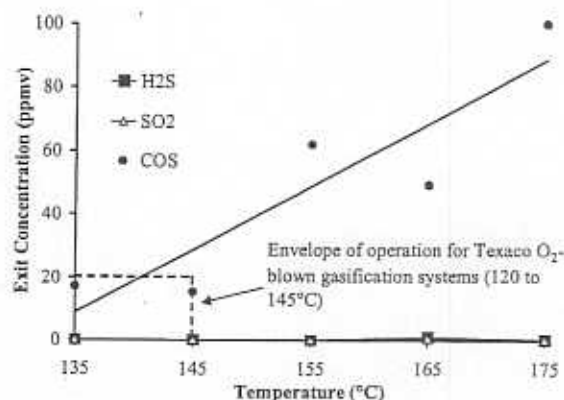


Figure 3. Sulfur exit concentrations from the desulfurizer for H₂S, SO₂, COS. Inlet conditions were a simulated Texaco O₂-blown gasifier gas with 1,000 ppmv H₂S at the inlet. H₂S:O₂ was 1:5, GHSV was 2,500 h⁻¹.

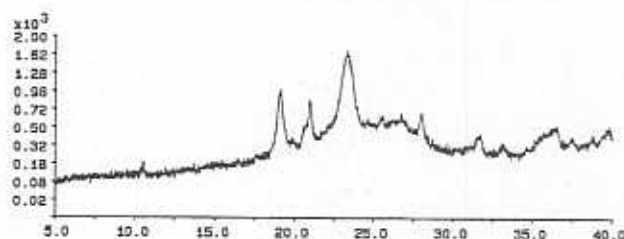


Figure 4. Powder x-ray diffraction pattern for elemental sulfur formed in the pores of the activated carbon catalyst after six hours online. Peaks located at 19.12°, 20.91° and 23.22° are consistent with orthorhombic sulfur formation.

Conclusions

From this investigation the following conclusions were drawn. In natural gas fuel processing systems activated carbon has the ability to selectively oxidize H₂S to less than 1.0 ppmv without appreciable side reaction occurring in the temperature range between 105 and 125°C. The activated carbon catalyst, in middle distillate fuel processing systems, demonstrated high sulfur selectivity; however, low conversions of O₂ and H₂S were observed. In coal-derived synthesis gas fuel processors, the activated carbon catalyst removed H₂S levels to less than 1.0 ppmv up to 175°C. However, above 145°C significant side reaction with CO occurred.

Acknowledgement

This work was supported by the Fuel Cell Product Line, U. S. Department of Energy, NETL. Mr. Lanny Golden is acknowledged for his dedication, enthusiasm and hard work on this project.

References

- (1) Petroleum Extension Service. Field Handling of Natural Gas, 3rd Ed., Univ. of Austin Texas Press, 1981; p. 73.
- (2) U. S. Mil spec Mil-T 83133E.
- (3) Ghosh, T. K. and Tollefson, E. L. *Can. J. Chem. Eng.*, 1986, 64 (12), 960.
- (4) Ghosh, T. K. and Tollefson, E. L. *Can. J. Chem. Eng.*, 1986, 64 (12), 969.
- (5) Kensell, W. and Leppin, D. "Review of the H₂S Direct Oxidation Process;" *Seventh GRI Sulfur Recovery Conference*, 1995.
- (6) Meyer, B.; Schiffer, H. P.; and Walter, H. *Proceedings ICCS '97*, Ziegler et al., Ed., 1997; pp. 1775-1778.
- (7) Royan, T. S. "Sulfur Recovery by Direct Oxidation Process;" *Gas Processing/Canada*, Jan.-Feb. 1972.